INHOMOGENEOUS GELS CROSSLINKED WITHIN SPINODAL REGION(Session III : Complex Fluids, The 1st Tohwa University International Meeting on Statistical Physics Theories, Experiments and Computer Simulations)

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Abstract. We consider theoretically the gels crosslinked in the early stage of spinodal decomposition. The inhomogenization of gel is 'recorded' as position dependent distribution of chain conformations due to the additional crosslinks. We analyze the stability of the inhomogeneous gel thus processed. Our study shows that the spinodal instability may still occur in inhomogeneous 'opaque' gel.

1. Introduction

In chemically crosslinked polymer gel the way how crosslinks are introduced has generally a strong influence upon thermodynamic properties of the gel, including spinodal instability. The intra-network crosslinks within spinodal decomposition can incessantly 'record' the inhomogeneous local deformation of gel as a so-called *permanent set* [1]. Our interest is in (i) how the intra-network crosslinking affects the dynamics of spinodal decomposition, and (ii) how is the thermodynamic stability of the resulting inhomogeneous gel.

2. Dynamics of thermodynamically unstable gel undergoing crosslinking reactions

We assume for simplicity that the gel undergoes only the unidirectional and periodic modulation induced by the fastest growing mode of spinodal decomposition. We take as a reference state of deformation the initial homogeneous gel. We denote by X the position of a material point of the network in the reference state.

For the elastic part of the free energy we take basically the model of permanent set in rubber theory[1]. We extend the use of this model[1] to allow for inhomogeneous deformations which include volumetric deformation as well as shear deformation. The evolution equation for the relative elongation ratio, $\lambda(X,t)$, is derived following the standard framework of non-equilibrium thermodynamics[2,3]. As for the evolution of the number density of elastically active chains, $\nu(X,t)$, we consider a kind of vulcanization reaction between the crosslinking agents which are attached chemically onto the network chains.

Intra-network crosslinking generally tends to stabilize the system by shifting the dominant growth mode of spinodal decomposition toward the larger wavelength ('red shift'). On the other hand, the progressive establishment of permanent set tends to resist the red shift. We sought for the condition where the latter effect dominates over the former. Figure 1(a) shows an example of the evolution for small rate of crosslinking. The inhomogeneity is already established before the wavelength of the fastest growth mode changes appreciably. We also did a comparative calculation (Figure 1(b)), where the parameters are the same as those in Figure 1(a) but the heterogeneity of permanent set is suppressed. $\lambda(X,t)$ is seen to catch up with the shift of the most unstable growth mode.

3. Phase instability of inhomogeneous chemical gel

We consider whether or not the inhomogeneously crosslinked gel is stable against the fluctuation of large wavelengths. For this purpose we prepared a model periodic gel which mimics the heterogeneously crosslinked network under the influence of spinodal decomposition (see Sec. 2). We analyzed the linear stability of the system with the aid of Bloch's theorem concerning the eigenvalue problem of periodic systems.

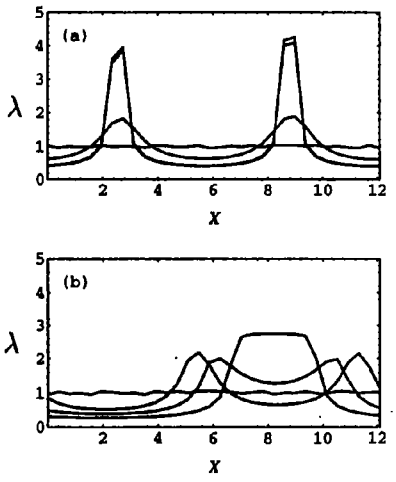

Figure 1: The evolution of the elongation ratio, λ, during spinodal decomposition that takes place simultaneously with irreversible crosslinking. (a)The dimensionless time of each curve is, in the increasing order of the peak height of the curves, $\tilde{t} = 0$, 348, 1435 and 4328, respectively. (b)The dimensionless time of each curve is, in the decreasing order of the minimum height of the curves, $\tilde{t} = 0$, 1435, 2501 and 4313, respectively.

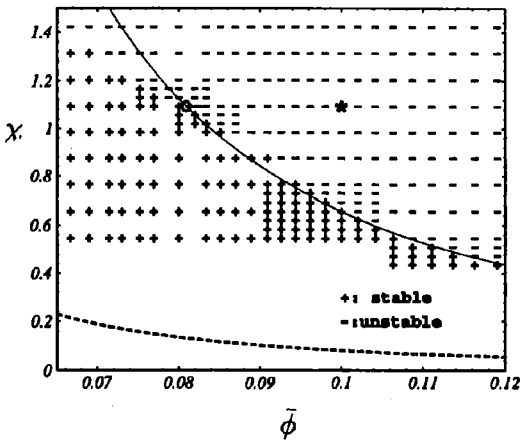

Figure 2: The stability diagram of the gel with periodically modulated permanent crosslinking.

The result is shown in the plane of interaction parameter χ and the mean volume fraction of gel, $\bar{\phi}$ (Figure 2) where (+) and (−), respectively, indicates stable and unstable state. The parameters at which the gel is crosslinked is shown by the asterisk. The thick dashed curve indicates the spinodal curve of the initial homogeneous gel before introducing permanent set. The increase of the overall crosslinking causes the shift of the spinodal curve appreciably towards the positive χ direction. It can thus happen that as opacity develops in gel in the early stage of crosslinking reaction, the system brings itself into a stable 'single phase' state at the end of reaction. On the other hand the effect of spatial inhomogeneity is thus shown to be small: We have also shown the spinodal curve of the *homogeneous* gel that has the *same* amount of crosslinks as the one studied above (the thin solid curve).

4. Conclusion

We have investigated the interplay between intra-network crosslinking and spinodal decomposition of gel. We demonstrated how the permanent set affects the inhomogeneity of network. In the latter half of the present work we have studied the possibility of spinodal decomposition of mesoscopically inhomogeneous gels that have already experienced spinodal instability in the course of crosslinking. From the stability analysis of a simple system we assert that the gel may exhibit swelling-deswelling transition like an ordinary homogeneous gel even if the gel has mesoscopic inhomogeneity.

References

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